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VIBRATIONAL PRODUCT STATES FROM REACTIONS OF CN(-) WITH THE HYD--ETC(U)

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# Vibrational product states from reactions of $\text{CN}^-$ with the hydrogen halides and hydrogen atoms

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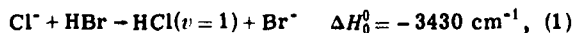
Infrared chemiluminescence is observed from the C-H stretch manifold  $\nu_3$  of HCN formed in the gas phase ion-molecule reactions:  $\text{CN}^- + \text{HX} \rightarrow \text{HCN}(\nu_3) + \text{X}^-$ , with  $(\text{X} = \text{Cl}, \text{Br}, \text{I})$ , and for  $\text{CN}^- + \text{H} \rightarrow \text{HCN}(\nu_3) + e^-$ . Qualitative information is also obtained for excitation in the bending mode. In each case some excitation is observed in the highest level allowed by energy conservation. Comparison with similar studies of the reactions  $\text{Cl}^- + \text{HX}$  shows that the stretching mode of the newly formed bond is less efficiently populated in the HCN case. Emission is observed from CNH (hydroisocyanic acid) formed in the reaction  $\text{CN}^- + \text{HI} \rightarrow \text{CNH}(\nu) + \text{I}^-$ .

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## I. INTRODUCTION

Reaction mechanisms are increasingly viewed as problems in reaction dynamics.<sup>1-5</sup> A vast effort has been made in the study of neutral, radical reactions and this is steadily being extended to include ions.<sup>6-19</sup> An important difference between neutral and ion reactions is the intermolecular potential. The potential between neutrals is only weakly attractive and generally features a barrier which must be surpassed for reaction to take place. In contrast, ion-molecule reactions feature potentials dominated by the attractive ion-dipole and ion-induced dipole terms and, consequently, pass through potential minima.<sup>11,12</sup> How will this fundamental difference in potential energy surfaces affect the reaction dynamics? One method to investigate this question is to determine the deposition of energy among the reaction products. Many ion reactions are quite fast and have large exothermicities.<sup>7</sup> It is likely that ion-molecule reaction products will be internally excited. If a pattern of energy disposal can be discerned, this information can be compared and contrasted to the wealth of data available for neutral reactions.

The reaction dynamics of ions has been studied in beams and reaction products have been observed in electronic emission spectroscopy.<sup>13,14</sup> Recently, the first observation of infrared chemiluminescence from an ion-molecule reaction was reported from this laboratory.<sup>15</sup> The flowing afterglow method<sup>16</sup> was adapted by addition of an IR detection system to observe the vibrational fluorescence from the products of ion reactions. A complete study of the product vibrational energy distribution of HCl produced in the reactions of  $\text{Cl}^-$  with HBr and HI was subsequently carried out by Zwier *et al.*<sup>17</sup>



The results reported there demonstrated the usefulness of the technique for obtaining quantitative information

about the vibrational states of the nascent product molecule.

In this paper we would like to apply our infrared chemiluminescence technique to ion reactions that produce polyatomic (rather than diatomic) molecules as products. The study of IR emission from polyatomic species is much more complicated than processes such as Reactions (1) or (2). Instead of the excitation being in just one vibrational mode as in HCl, (3N-6) modes are available for an N atom species, (3N-5) if the molecule is linear. We would like to know which of the many internal modes are populated in a vibrationally excited polyatomic product born in an ion-molecule reaction. How much energy is deposited into a particular mode?

A host of problems accompany the study of emission from a polyatomic species. For instance, the spectroscopy of the molecule becomes more complicated and the emission lines may be difficult to sort out and assign. Worse yet, the energy may scramble via intramolecular pathways so that the resulting emission bears little resemblance to the initial product state distribution. In an extreme case, the internal energy may rapidly leak out by deactivation of a low frequency vibrational mode by collision with other species in the flow tube resulting in no emission at all.

As a first step in the study of polyatomic reaction products, we have chosen a triatomic molecule. This molecule must be selected to minimize the spectroscopic problems noted above and to meet certain requirements imposed by the flowing afterglow technique.

We selected HCN. This molecule has several attractive spectroscopic features:

(1) The first attraction is that the ( $\nu_3$ ) mode—the H-CN stretch—is well separated from the nearest energy levels. (The particular vibrational modes are labeled by  $\nu_n$  while  $\nu_n$  designates the number of quanta in mode  $\nu_n$ . We adopt the notation  $\nu_1$  for the  $\text{C}\equiv\text{N}$  stretch,  $\nu_2$  for the H-C-N bend, and  $\nu_3$  for the C-H stretch.) The result is that, as in the case of the  $\nu_3=1$  state of  $\text{CO}_2$ , a negligible amount of vibrational deactivation should be caused by collisions with the 0.3 Torr of He in the ob-

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TABLE I. Reactions, rates and exothermicities.<sup>a</sup>

Reaction	$\Delta H_0^0$ kcal mol <sup>-1</sup>	$\Delta H_0^0$ cm <sup>-1</sup>	$k$ (experimental) cm <sup>3</sup> s <sup>-1</sup>	$k$ (ADO) cm <sup>3</sup> s <sup>-1</sup>
$\text{CN}^- + \text{HF} \rightarrow \text{HCN} + \text{F}^-$	20.4	7 150	...	...
$\text{CN}^- + \text{HCl} \rightarrow \text{HCN} + \text{Cl}^-$	-17.7	-6 180	3.0(-9)	1.5(-9)
$\text{CN}^- + \text{HBr} \rightarrow \text{HCN} + \text{Br}^-$	-27.4	-9 600	2.4(-9)	1.3(-9)
$\text{CN}^- + \text{HI} \rightarrow \text{HCN} + \text{I}^-$	-36.7	-12 800	1.3(-9)	1.3(-9)
$\text{CN}^- + \text{H} \rightarrow \text{HCN} + e^-$	-36.5	-12 800	1.3(-9)	...
$\text{CN}^- + \text{DI} \rightarrow \text{DCN} + \text{I}^-$	-37.1	-13 000	...	...
$\text{Cl}^- + \text{HBr} \rightarrow \text{HCl} + \text{Br}^-$	-9.8	-3 430	7.5(-10)	...
$\text{Cl}^- + \text{HI} \rightarrow \text{HCl} + \text{I}^-$	-19.0	-6 650	6.3(-10)	...
$\text{Cl}^- + \text{H} \rightarrow \text{HCl} + e^-$	-18.9	-6 610	9.6(-10)	...

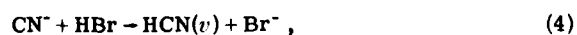
<sup>a</sup>The tabulated rate constants abbreviate the exponent; the constant for  $\text{CN}^-$  reacting with HCl is  $3.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . The average dipole orientations approximation (ADO) is taken from Ref. 63. The rate constant for  $\text{CN}^- + \text{H}$  is taken from Fehsenfeld (Ref. 47) while Zwier *et al.* (Ref. 17) have supplied data for the last three  $\text{Cl}^-$  reactions. The uncertainty in  $\Delta H_0^0$  for all of the  $\text{CN}^-$  reactions is  $\pm 2.6 \text{ kcal mol}^{-1}$  or  $\pm 900 \text{ cm}^{-1}$ .

servation time of about 0.5 msec.<sup>18-20</sup>

(2) The H-CN band emits strongly, having an intensity about twice that of HCl. This is crucial in order that the IR chemiluminescence can be detected.

(3) One major advantage of studying HCN instead of, say,  $\text{CO}_2$  is that the  $\nu_3$  mode of HCN is very anharmonic, being about  $100 \text{ cm}^{-1}$ . This anharmonicity is greater than the rotational-vibrational envelope of the band. So it will be possible to separate emission from, say, the (003)-(002) transition and that of (002)-(001) using interference filters. This is not possible for the (00<sub>n</sub>) levels of  $\text{CO}_2$ .

The ion-molecule reactions which are the subject of this paper are the proton abstraction reactions



and the associative detachment reaction



This set of reactions has several attractive features.

(1) Reactions (3)-(6) are all very fast and proceed on about every collision as shown in Table I.

(2) The reagent ion  $\text{CN}^-$  can be produced in large quantities (ion densities of  $10^8 \text{ cm}^{-3}$ ) from several different precursors.

(3) Any reactions involving neutral CN radicals will be negligibly slow<sup>21</sup> compared with those of  $\text{CN}^-$ .

We report in this paper the relative populations of  $\text{HCN}(00\nu_3)$  produced by the ion reactions (3)-(6). Table I shows the exothermicities of Reactions (3)-(6) are small enough to excite the H-CN stretch over the range ( $\nu_3 = 1$ ) to ( $\nu_3 = 4$ ). It is much more difficult to study the degree of excitation of the  $\nu_1$  and the  $\nu_2$  modes. By the appropriate use of deactivation and energy transfer techniques, we have obtained some information on the population in the bending mode.

A totally unexpected result is that the reaction be-

tween  $\text{CN}^-$  and HI produces CNH as well as HCN. HCN is the only product observed in the reaction of  $\text{CN}^-$  with H atoms even though Reactions (5) and (6) have about the same exothermicities (Table I). This is of great interest as CNH has been observed in interstellar space.<sup>22-24</sup>

## II. EXPERIMENTAL

A summary of the experimental conditions used for the  $\text{CN}^-$  reactions is given here. A more complete description of the apparatus and tests on its performance is given in Ref. 17.

### A. The flowing afterglow apparatus

The flowing afterglow apparatus used for the present experiments is depicted in Fig. 1. At the upstream end, helium (or argon) carrier gas enters via the ionizer assembly. Electron impact produces helium ions, metastables, and slow electrons which subsequently react with the reagents introduced through the ion precursor inlet to produce reactant ions. The mixture is allowed to flow downstream for approximately 40 cm before the addition of the neutral reagents; the flow velocity of the buffer gas is  $8 \times 10^3 \text{ cm s}^{-1}$ . This corresponds to about  $2 \times 10^4$  collisions with the He buffer gas, allowing for the establishment of clean flow conditions and the completion of the reactions producing the desired ions. This large number of collisions tends to thermally equilibrate the ions. Neutral reagents can be admitted either through the radial inlets or the movable injector. Both provide for a uniform addition of the reagent across the cross section of the flow tube which in turn allows us to characterize the time origin for the reaction. The ions are then sampled through the nose cone which has a 0.25 mm orifice and is held at +3 V to attract the negative ions. Finally mass analysis is achieved with a quadrupole mass filter and the ions are detected either with a ceratron particle counter or by measuring the current on a Faraday plate.

### B. Infrared detection

The usual flowing afterglow apparatus<sup>16</sup> has two modifications to allow for the detection of infrared chemiluminescence. One is an observation window normal to the direction of flow which is installed near the down-

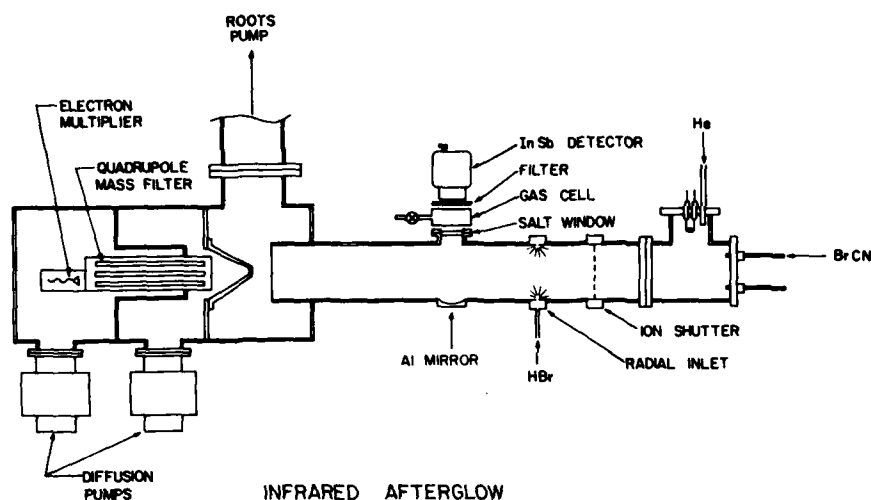


FIG. 1. A schematic of the flowing afterglow apparatus.

stream end of the flow tube. The window is placed roughly tangent to the inside wall of the flow tube (about 4 cm from the axis). This allows light collection from a large volume and hence improves the signal-to-noise ratio. A 10 cm focal length aluminum mirror lies opposite the window to further increase light gathering. In practice neutral inlets at various distances from the window are used to allow emission signals to be recorded at different times from the origin of the reaction.

The second modification is the placement of a tungsten mesh across the flow tube upstream of the neutral inlets. This is the ion shutter shown in Fig. 1. A potential of about 10 V applied to the mesh interrupts the flow of ions. Square wave modulation of the potential (0–10 V, 200 Hz) on the mesh results in the formation of packets of ions, thus modulating the products of ion reactions. Since neutral reactants will not be affected, this method enables us to distinguish emission of products of ion-molecule reactions from background emission. This modulation technique is crucial to our experiment as the electron impact source also produces excited neutral species which can react with constituents present in the flow tube. Use of these voltages on the tungsten mesh achieved about 50% modulation of the ions. Higher mesh voltages may cause electron detachment from the negative ions at the ion shutter. The emission signals reported in this paper did not depend on the mesh voltage, modulation frequency, or duty cycle, in the region near the values used.

A 1.27 cm diam 77 K InSb detector was used in conjunction with a set of interference filters to resolve and detect infrared emission. The output from the InSb detector was amplified and signal averaged. The resulting modulated waveform was then integrated to improve the signal-to-noise ratio and displayed on an X-Y recorder. A representative IR emission spectrum is shown in Fig. 2; the signal is from  $\text{HCN}(00n)$  where  $n=1, 2$ , and 3. The  $\text{HCN}$  is produced by reaction of  $\text{CN}^-$  with  $\text{HBr}$ . In this experiment the ions are stopped by the ion shutter at  $t=0$ . Subsequent depletion of the excited reaction products appears as a decrease in the IR signal at  $t=2$  or 3 msec. The integral of the dip in the IR signal is

also displayed. The increased signal-to-noise ratio is evident.

### C. $\text{CN}^-$ production

One of the requirements for detection of vibrational chemiluminescence from products of ion-molecule reactions is to begin with very high densities of reactant ions (about  $10^8 \text{ cm}^{-3}$ ). This corresponds to roughly four orders of magnitude higher densities than is typical in standard flowing afterglow experiments. Not all precursor reagents provide the required number of ions. The  $\text{CN}^-$  must also be the only reactive ion present in the flow tube. Any other ions, positive or negative, which undergo reactions could produce interfering sources of emission.

Two molecules were used as precursors to  $\text{CN}^-$ —cyanogen ( $\text{C}_2\text{N}_2$ ) and cyanogen bromide ( $\text{BrCN}$ ). Neither was perfect; however the chemiluminescence results obtained did not depend on which reagent was used. About 1 or 2 pA of ion current ( $\text{CN}^-$  at  $m/z=26$ ) was measured

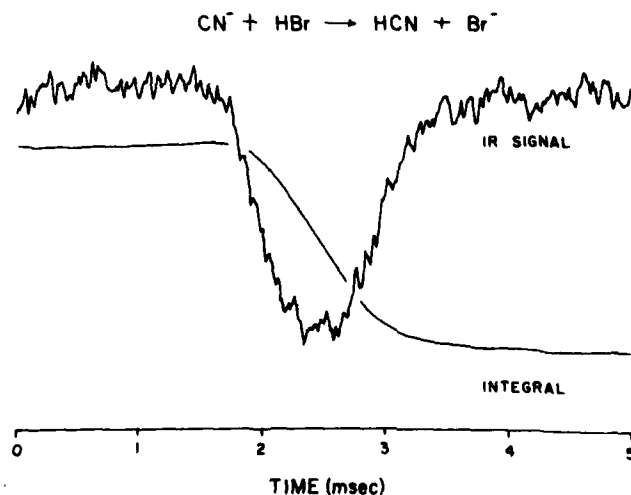


FIG. 2. A typical IR emission signal and its integral in the  $3000 \text{ cm}^{-1}$  region after 10 min of signal averaging.

on the Faraday plate when  $\text{C}_2\text{N}_2$  was used as the ion source. This was sufficient to observe a reasonable emission signal from HCN after 128 K sweeps (roughly 10 min of signal averaging). The only negative ion produced from  $\text{C}_2\text{N}_2$  is  $\text{CN}^-$ . The positive ion spectrum is rather complex consisting of  $\text{C}_2\text{N}_2^+$ ,  $\text{C}_2\text{N}_4^+$ ,  $\text{C}_4\text{N}_4^+$ , and so on to high mass polymeric ions. As HCl is added to the flow tube,  $\text{CN}^-$  disappears and  $\text{Cl}^-$  appears indicating that Reaction (3) occurs. Since this reaction is very fast, only small flows (low pressures) of HCl are required to achieve complete reaction in the 5–11 cm before the IR detector (a throughput  $Q$  of 1 STP  $\text{cm}^3 \text{s}^{-1}$  or 2.3 mTorr was sufficient). No reactions of the positive ions were observed when HCl was added to the apparatus with  $\text{C}_2\text{N}_2$  as the ion precursor. However, both HBr and HI react with  $\text{C}_2\text{N}_2$  positive ions. This is an undesirable situation since such reactions may produce emitting species which will be modulated.

Cyanogen bromide (BrCN) was used as a second source of  $\text{CN}^-$ . BrCN produces about four times as much  $\text{CN}^-$  ions as cyanogen. Unfortunately,  $\text{CN}^-$  is not the only negative ion produced; about 10% of the total negative ion intensity is  $\text{Br}^-$ . Although  $\text{Br}^-$  is only a small fraction of the negative ions present, its reactions with HI and H will result in vibrationally excited HBr (the analogous reactions with HCl and HBr are not exothermic). Emission from  $\text{HBr}(v)$  can be excluded by using a fixed frequency filter which blocks light below 2800  $\text{cm}^{-1}$ .

The positive ion spectrum produced by BrCN consists of three sets of peaks due to  $\text{Br}^+$ ,  $\text{HCNBr}^+$ , and  $\text{CNBr}_2^+$ . Addition of any reagent (HCl, HBr, HI) causes the  $\text{CNBr}_2^+$  peak to decrease and the  $\text{HCNBr}^+$  peak to increase. Furthermore, IR radiation can easily be de-

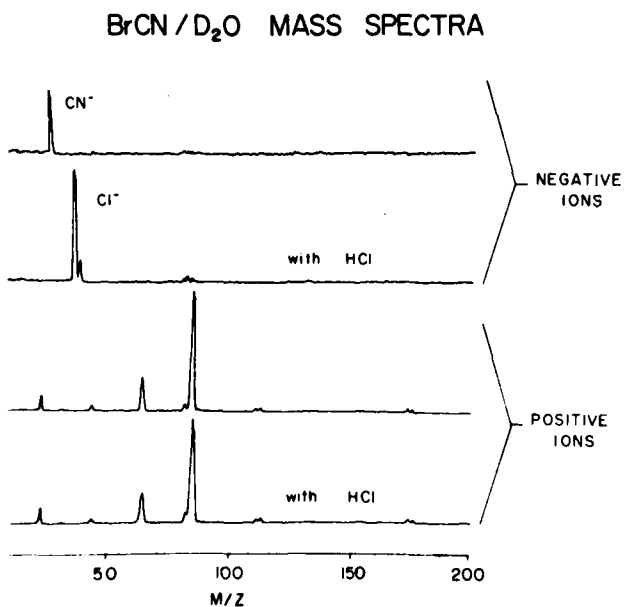


FIG. 3. Mass spectra of both positive and negative ions in the flow tube before and after addition of HCl reactant gas.  $\text{D}_2\text{O}$  is present (0.2 mTorr) to ensure that the only change in the spectra is from the desired negative ion-molecule reaction.

TABLE II. Neutral reactions with  $\text{CN}^-$ .

	$\Delta H_0^0$ $\text{kcal mol}^{-1}$	$\Delta H_0^0$ $\text{cm}^{-1}$	$k$ $\text{cm}^3 \text{s}^{-1}$
$\text{CN} + \text{HF} \rightarrow \text{HCN} + \text{F}$	10.7	3750	...
$\text{CN} + \text{HCl} \rightarrow \text{HCN} + \text{Cl}$	-22.4	-7830	3.7(-14)
$\text{CN} + \text{HBr} \rightarrow \text{HCN} + \text{Br}$	-38.0	-13300	3.7(-13)
$\text{CN} + \text{HI} \rightarrow \text{HCN} + \text{I}$	-54.2	-19000	7.6(-12)

\*Rate constants were measured by G. Roden (Ref. 21).

tected without the addition of any neutral reagent whatsoever. The use of filters enabled us to narrow the frequency range of the emission to 3200–3400  $\text{cm}^{-1}$  and 1800–2000  $\text{cm}^{-1}$ . It was noted that upon the addition of  $\text{D}_2\text{O}$  to the flow tube,  $\text{DCNBr}^+$  was present in the flow tube instead of  $\text{HCNBr}^+$ . Concurrently, the IR emission shifted into the 2200–2500  $\text{cm}^{-1}$  range. We attribute the IR signals to emission from the C–H stretch and  $\text{C}\equiv\text{N}$  stretch of  $\text{HCNBr}^+$ . Addition of  $\text{D}_2\text{O}$  to the system shifts the interfering IR signals to a region of the spectrum where they can be conveniently blocked with the appropriate filter.

Consequently, about 0.2 mTorr of  $\text{D}_2\text{O}$  was added to the flow tube upstream from the neutral inlets for the majority of the experiments in which BrCN was used as a precursor to  $\text{CN}^-$ . The positive ion mass spectrum then consisted entirely of the clusters  $\text{D}_3\text{O}^+(\text{D}_2\text{O})_n$  and was unaffected by the addition of any neutral reactants. The mass spectra for both positive and negative ions produced in the mixture BrCN/ $\text{D}_2\text{O}$  are displayed in Fig. 3. A filter which cut off below 2800  $\text{cm}^{-1}$  was always used when emission from vibrationally excited HCN was examined. In several instances (notably in the energy transfer studies to OCS and for the reaction of  $\text{CN}^-$  with DI) when emission was expected below 2800  $\text{cm}^{-1}$ ,  $\text{H}_2\text{O}$  was added to the flow tube and blocking filters above 3000  $\text{cm}^{-1}$  were employed.

Although the addition of  $\text{D}_2\text{O}$  solves the problem of interfering emission due to positive ion reactions, it is important to determine if  $\text{D}_2\text{O}$  will vibrationally deactivate the newly formed HCN. In practice the pressure of  $\text{D}_2\text{O}$  was 1000 times lower than that of the He buffer gas. The nascent HCN would suffer fewer than five collisions with  $\text{D}_2\text{O}$  before being observed at the IR detector; this suggests that deactivation by  $\text{D}_2\text{O}$  will not be a problem. The same relative emission intensities were observed using  $\text{C}_2\text{N}_2$  or BrCN as the source of  $\text{CN}^-$ , so neither the positive ion chemistry in  $\text{C}_2\text{N}_2$  nor the addition of  $\text{D}_2\text{O}$  to BrCN affects emission.

The  $\text{CN}^-$  ions which might be detached by the mesh voltage form a modulated source of CN. These may react to form vibrationally excited HCN. Vibrational emission due to a similar mechanism was observed by Zwier *et al.*<sup>17</sup> The rates of reaction of CN are roughly 3 to 4 orders of magnitude slower than those of the ion-molecule reactions as shown by the rate constants<sup>21</sup> listed in Table II. This implies that a detectable quantity of "radical-generated" HCN cannot be produced in the time available. There is no effect on the IR signal as the mesh voltage is increased. Hence radical reac-

TABLE III. Spectroscopic information for HCN and CNH.

$$\nu = E - E_0 = \omega_1^0 \nu_1 + \omega_2^0 \nu_2 + \omega_3^0 \nu_3 - X_{11} \nu_1^2 - X_{22} \nu_2^2 - X_{33} \nu_3^2 - X_{12} \nu_1 \nu_2 - X_{13} \nu_1 \nu_3 - X_{23} \nu_2 \nu_3 - g_{22} \nu_2^2.$$

	HCN <sup>a</sup> (cm <sup>-1</sup> )	DCN <sup>a</sup> (cm <sup>-1</sup> )	CNH		CND	
			Gas phase frequencies (cm <sup>-1</sup> )	Ar matrix frequencies (cm <sup>-1</sup> )	Gas phase frequencies (cm <sup>-1</sup> )	Ar matrix frequencies (cm <sup>-1</sup> )
$\omega_1^0$	2107.06	1932.37	$\nu_1$ ...	2029.	...	1940.
$\omega_2^0$	710.77	569.22	$\nu_2$ ...	477.	...	374.
$\omega_3^0$	3363.90	2650.56	$\nu_3$ 3652.9	3620.	2780.4	2769.
$X_{11}$	10.45	7.10	$B_0$ 1.51211		1.27264	
$X_{22}$	2.50	2.09				
$X_{33}$	52.50	20.23				
$X_{12}$	2.90	-2.73				
$X_{13}$	14.43	32.88				
$X_{23}$	19.19	15.71				
$B_0$	1.47791	1.20770				
$g_{22}$	-3.63	-2.00				

<sup>a</sup>Infrared Absorbance Intensities:for HCN:  $S_1 = 1 \text{ atm}^{-1} \text{ cm}^{-2}$ ;  $S_2 = 257 \text{ atm}^{-1} \text{ cm}^{-2}$ ;  $S_3 = 238 \text{ atm}^{-1} \text{ cm}^{-2}$ .for DCN:  $S_1 = 13 \text{ atm}^{-1} \text{ cm}^{-2}$ ;  $S_2 = 68 \text{ atm}^{-1} \text{ cm}^{-2}$ ;  $S_3 = 121 \text{ atm}^{-1} \text{ cm}^{-2}$ .

tions are of no consequence for the present study.

Electronic grade HCl (99.9%), high purity HBr (99%), HI (98%), and OCS (97.5%) were obtained from Matheson and used without further purification (except for the HI used in the kinetics measurements which was purified to remove H<sub>2</sub>). The carrier gas was passed through a liquid nitrogen cold trap before being used. Cyanogen (Matheson 98.5%) was used without purification while cyanogen bromide (Aldrich 97%) was distilled from sodium prior to use. HCN was prepared from sodium cyanide and sulfuric acid.<sup>25</sup> Hydrogen atoms were produced in a thermal dissociator by passing high purity H<sub>2</sub> over a hot tungsten filament in a water cooled glass chamber which had been coated with boric acid (alternatively halocarbon wax<sup>26</sup>) to inhibit surface recombination.<sup>27</sup>

### III. HCN PROPERTIES

#### A. Thermochemistry

The amount of energy available for internal excitation of product HCN formed in Reactions (3)–(6) depends on the exothermicities of these reactions. These quantities are calculated using Eq. (7) and are listed in Table I:

$$\Delta H_0^0 = EA(\text{CN}) - D_0^0(\text{H-CN}) + D_0^0(\text{HX}) - EA(\text{X}). \quad (7)$$

The electron affinity of CN is obtained from the photoionization<sup>28</sup> of HCN and is  $EA(\text{CN}) = 3.82 \pm 0.02 \text{ eV}$ . The dissociation energy  $D_0^0(\text{HCN}) = 5.40 \pm 0.09 \text{ eV}$  and is calculated from the heats of formation<sup>29</sup> of HCN, H, and CN. The dissociation energies of the hydrogen halides can be obtained from Huber and Herzberg<sup>30</sup> while the electron affinities of the halide ions are available from Hotop and Lineberger.<sup>31</sup> The energies of the reactions are listed in Table I.

Exothermicities for the same reactions producing CNH will differ by the relative stability of CNH versus HCN. This energy gap has been calculated by several groups<sup>32,33</sup> but only sketchy experimental data are available.<sup>34</sup> A reasonable figure for this isomerization energy is about 15 kcal mol<sup>-1</sup> or 0.63 eV.<sup>33</sup> Thus roughly 5200 cm<sup>-1</sup> less energy is available for internal excitation of CNH than for HCN in all of these reactions. Only reactions of CN<sup>-</sup> with HI and H should release enough energy to produce vibrationally excited CNH.

#### B. Spectroscopy

The values of the spectroscopic constants for HCN and DCN are available from Allen *et al.*<sup>35</sup> A table of these is provided for convenience (Table III). The three fundamental frequencies are  $\nu_1 = 2096.6$ ,  $\nu_2 = 708.3$ , and  $\nu_3 = 3311.4 \text{ cm}^{-1}$ . Important values for the present experiments are the anharmonicity,  $X_{33} = 52.5 \text{ cm}^{-1}$  and the rotational constant,  $B_e = 1.48 \text{ cm}^{-1}$ . A large anharmonicity factor for the C–H stretch in comparison to a relatively modest rotation constant indicates that emission from the sequence levels in this mode may be separable by the use of narrow bandpass filters. Although the *P* lines of one transition overlap with the *R* lines of the next, a deconvolution procedure is possible. Note that the anharmonicity factor of  $X_{22} = 2.5 \text{ cm}^{-1}$  makes a similar prospect impossible for the bending mode  $\nu_2$  under present experimental conditions. This problem also exists for the C≡N stretch  $\nu_1$ .

The infrared intensities for the modes of HCN have been measured by Kim and King.<sup>36</sup> Their values are reported in Table III. Note that the absorption intensities<sup>37</sup> for the C–H stretch and the bend are reasonably large: 238 atm<sup>-1</sup> cm<sup>-2</sup> and 257 atm<sup>-1</sup> cm<sup>-2</sup>, respectively, (com-

pared to  $174 \text{ atm}^{-1} \text{ cm}^{-2}$  for  $\text{HCl}^{38}$ ). Unfortunately, the very small value for the  $\text{C}\equiv\text{N}$  stretch ( $\nu_1$ ) will make it impossible to observe direct emission from this mode. As mentioned earlier, the small anharmonicity constant will not allow us to separate the emission from the various levels of the bend  $\nu_2$ . In addition, though the absorption strength is about the same, the Einstein  $A$  coefficient varies as  $\nu^3$  so that the IR emission from the bending mode can be expected to be smaller by a factor of 0.05 than the emission from the  $\text{C}-\text{H}$  stretch. Consequently, it was not surprising that no signal could be detected in the  $700 \text{ cm}^{-1}$  region.

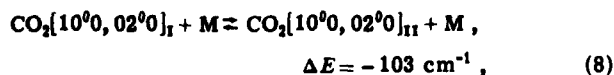
The infrared spectrum of  $\text{CNH}$  was first obtained by Milligan and Jacox<sup>39</sup> who photolyzed methyl azide in an argon matrix. Gas phase emission spectra were obtained by Arrington and Ogryzlo<sup>40</sup> for  $\text{CNH}$  and  $\text{CND}$  but only for the  $\nu_3$  mode. At  $3653 \text{ cm}^{-1}$ , the  $\text{N}-\text{H}$  stretch can be easily distinguished from the  $\text{C}-\text{H}$  stretch with our interference filters. The other spectral constants are collected in Table III.

We must know how intense  $\text{CNH}$  infrared emission is. We can estimate the absorption strength of the ( $\nu_3=1$ ) - ( $\nu_3=0$ ) of  $\text{CNH}$  relative to the same transition in  $\text{HCN}$ . This can be done by calculating the ratio of the respective Einstein  $A$  coefficients  $A_{001}(\text{CNH})/A_{001}(\text{HCN})$ . Our value for this ratio is based on an *ab initio* GVB(PP) calculation of the dipole moment derivatives for both  $\text{HCN}$  and  $\text{CNH}$ . These computations were carried out by Dr. J. J. Wendoloski of the NRCC and are outlined in Appendix A. He finds the ratio  $A_{001}(\text{CNH})/A_{001}(\text{HCN})$  to be 4.0. Hence, emission from the  $\text{N}-\text{H}$  stretch of  $\text{CNH}$  should be roughly four times as bright as emission of the  $\text{C}-\text{H}$  stretch of  $\text{HCN}$ .

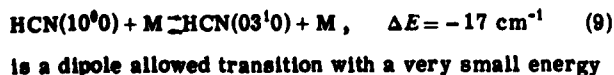
### C. Vibrational relaxation of $\text{HCN}$

$\text{HCN}$  is a triatomic molecule in which vibrational relaxation is expected to be similar to that of  $\text{CO}_2$ . The most important difference is that in energy relaxation experiments with  $\text{CO}_2$ , collisions between  $\text{CO}_2$  molecules play an important role in holding the bending and stretching levels in equilibrium. In contrast, these flowing afterglow experiments have the concentration of  $\text{HCN}$  molecules so low that there are no  $\text{HCN}-\text{HCN}$  collisions between the time of formation of the  $\text{HCN}$  and the observation of the IR emission.

In the case of  $\text{CO}_2$ , the bending and stretching levels are in Fermi resonance and are connected by very fast collisional processes such as

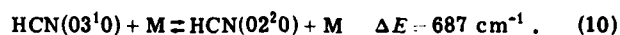


with  $k_8$  being about  $1 \times 10^6 \text{ sec}^{-1} \text{ Torr}^{-1}$  for He and varying little with the collision partner.<sup>41</sup> The  $(100)$  state of  $\text{HCN}$  is  $\Sigma^+$ , whereas the states  $(03^10)$  and  $(03^30)$  are  $\Pi$  and  $\Phi$ , respectively. Even though these states are nearly degenerate, there is no Fermi coupling as they have different symmetries. However, the process



defect. It is expected to be very fast and to equilibrate the  $(10^00)$  and  $(03^10)$  levels before the newly formed  $\text{HCN}$  is detected. This energy transfer [Reaction (9)] will be discussed in Sec. IV G.

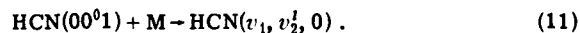
In the present experiment, deactivation will have to occur by processes such as



It is not known how fast these processes will occur for  $\text{HCN}$ . By analogy with the deactivation of the  $(01^10)$  level of  $\text{CO}_2$  at  $667 \text{ cm}^{-1}$ , one might expect that such a process would take about 1 msec with 0.3 Torr of He, about 10 msec with 0.3 Torr of Ar, and about 0.1 msec with this pressure of  $\text{H}_2$ .<sup>42,43</sup>

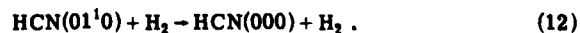
Clearly this argument applies to whether the  $(01^10)$  mode will be retained, or collisionally deactivated before it can be observed. In fact, this analogy holds quite well and it proved to be possible either to retain or to deactivate the bending mode before the observation time by a judicious choice of carrier gas. Recall that it takes about 0.5 msec for the product  $\text{HCN}$  molecules to travel downstream to the InSb IR detector.

The  $(00^01)$  mode of  $\text{CO}_2$  is relaxed very differently from the  $(01^10)$  mode of  $\text{CO}_2$ ; energy transfer probably taking place principally to the  $(11^10)$  level which is  $270 \text{ cm}^{-1}$  away. Unlike the relaxation of the  $(01^10)$  level, that of the  $(00^01)$  level does not depend greatly on the collision partner.<sup>44</sup> An analogous process is to be expected for  $\text{HCN}$  with



If the level concerned is the  $(11^10)$  or the  $(040)$ ,  $\Delta E$  is about  $500 \text{ cm}^{-1}$  exothermic; if it is the  $(050)$ , the  $\Delta E$  is about  $200 \text{ cm}^{-1}$  endothermic. Considering that a vibration involving H is concerned but the energy gap is rather larger than in  $\text{CO}_2$ , values for  $k_{11}$  in the region of  $200 \text{ sec}^{-1} \text{ Torr}^{-1}$  would be anticipated. McGarvey *et al.*<sup>45</sup> gave the rate constant as  $<100 \text{ sec}^{-1} \text{ Torr}^{-1}$  for M equals Ar or He and  $<200 \text{ sec}^{-1} \text{ Torr}^{-1}$  for M =  $\text{H}_2$ , while the recent work of Peterson and Smith<sup>19</sup> gave  $k_{11} = 250 \pm 30 \text{ sec}^{-1} \text{ Torr}^{-1}$  for both Ar and He.

Using the higher rate constant for M = He, we see that about 10% of the  $(00^01)$  level of  $\text{HCN}$  may be deactivated by He between the point of its formation and when we observe it. This is within our experimental error. The figures for M =  $\text{H}_2$  are a good indication that adding a judicious amount of  $\text{H}_2$  will deactivate the  $(01^10)$  vibration while having a negligible effect on the  $(001)$  level. This has proved to be the case, since



We do not have information on the relaxation of  $\text{CNH}$ . We expect a similar picture to that of  $\text{HCN}$  with the  $\text{H}-\text{NC}$  stretch readily observable just as is the  $\text{H}-\text{CN}$  stretch.

## IV. RESULTS

Ideally, it would be desirable to obtain a complete description of the vibrational state distribution for  $\text{HCN}$  produced by Reactions (3)–(6). Unfortunately, even for

this triatomic, such an endeavor is not possible with the present apparatus. However, a number of interesting results can be obtained when qualitatively different modes are available in the exit channel of the reaction.

(1) The relative populations of the  $\nu_3$  mode of product HCN molecules in Reactions (3)–(6) are determined.

(2) Considerable excitation in the HCN bending mode  $\nu_2$  is observed.

(3) Hydroisocyanic acid CNH is detected as a reaction product.

(4) Order of magnitude rate constants for the deactivation of  $\text{HCN}(01^10)$  by He, Ar, and  $\text{H}_2$  are found.

(5) Reaction rate constants for  $\text{HX} + \text{CN}^- \rightarrow \text{HCN} + \text{X}^-$  are presented.

(6) Energy transfer from  $\text{HCN}(\nu)$  to OCS is observed.

#### A. Analysis of data

Before embarking on a discussion of the findings, we present a brief description of the analysis by which the results are extracted.

Frequency selectivity in these experiments was obtained by using fixed interference filters which had a bandpass width of roughly  $150 \text{ cm}^{-1}$  and by the use of a 5 cm path length gas cell filled with 10 Torr of HCN. Figure 1 shows this gas cell placed between the observation window and the InSb IR detector. This will be referred to as the cold gas cell.

The anharmonicity of the C–H stretching mode depends also on the number of quanta in the bending mode through the term  $X_{23}$  ( $19 \text{ cm}^{-1}$  as shown in Table III). Thus, with an appreciable number of quanta in  $\nu_2$ , this contribution from the cross term is comparable to that from the term  $X_{33}$ . Under the conditions of our experiment, the bending vibrations were shown to be relaxed before the observation station using helium and helium/hydrogen mixtures as carrier gases. In these circumstances, contributions from the  $X_{23}$  cross term do not arise. The sequence bands in  $\nu_3$  of HCN are separated by an amount  $\Delta$ . This can be evaluated from Table III,  $\Delta = 2X_{33}$  as  $105 \text{ cm}^{-1}$ . Thus, the filters used allow us to separate the transitions of  $\text{HCN}(\nu_3 + 1) - \text{HCN}(\nu_3)$ , where  $\nu_3 = 3, 2, 1$ , or 0. (We specify only  $\nu_3$  when the quantum numbers of  $\nu_1$  and  $\nu_2$  are irrelevant.)

The use of fixed frequency interference filters can best be described by an example, say Reaction (3). Table I indicates that  $6200 \text{ cm}^{-1}$  ( $\pm 900 \text{ cm}^{-1}$ ) is available to be partitioned into translational energy or rotation–vibration excitation of HCN. Consider first the emission intensity observed under deactivating circumstances when  $\nu_1$  and  $\nu_2$  are relaxed. In this case the only states of HCN which are possible are  $(00^00)$ ,  $(00^01)$ , and  $(00^02)$ . If  $N(001)$  is the number of HCN molecules in the  $(00^01)$  state within view of the InSb detector and  $A(001)$  is the corresponding Einstein A coefficient, the integrated intensity  $I$  is

$$I = A(001)N(001) + A(002)N(002).$$

When a fixed frequency filter (say filter  $f$ ) is placed

before the InSb detector, the observed intensity  $I(f)$  is smaller:

$$I(f) = T(f, 1)A(001)N(001) + T(f, 2)A(002)N(002).$$

The  $T$  coefficients characterize the filter, i.e.,  $T(f, 2)$  is the fraction of the  $(00^02) \rightarrow (00^01)$  intensity transmitted by filter  $f$ . In general the amount of light passing through a filter  $f$  can be written

$$I(f) = \sum_{\nu_3} T(f, \nu_3)A(00\nu_3)N(00\nu_3).$$

If the  $\nu_1$  and  $\nu_2$  modes are not relaxed, the summation must be extended to include them. We can write this as

$$I(f) = \sum_{\nu_3} T(f, \nu_3)A(\nu_3)N(00\nu_3). \quad (13)$$

The quantity  $A(\nu_3)$  is just the ratio of the spontaneous emission coefficients for the transition  $(\nu_3) \rightarrow (\nu_3 - 1)$  to that for  $(1) \rightarrow (0)$ . The ratios  $A(\nu_3)$  are discussed in Appendix A.

Knowing the transmission functions  $T(f, \nu_3)$  for a set of filters and the Einstein coefficients, we measure  $I(f)$  and invert Eq. (13) to find  $N(00\nu_3)$ . The normalization of the  $N(00\nu_3)$  is arbitrary. We must measure the intensity with as many different filters as the maximum excitation of  $\nu_3$ . In our case this implies that four filters are required for the most exothermic reaction (5). It should be pointed out that the numbers obtained via the above analysis are expected to be accurate to  $\pm 25\%$ . A major source of error is the accuracy of the angle dependence of the transmission through the filters.

The transmission of each rotational line of the  $\nu_3 \rightarrow \nu_3 - 1$  transition through each filter must be computed in order to construct the transmission coefficients,  $T(f, \nu_3)$ . A complication arises from the large solid angle of light collected by our detector. Although advantageous for signal to noise, this has the drawback of distorting the transmission curves for the filters because the transmission depends on the angle of incidence of the incoming light. Increasing the angle from the normal to the filter shifts its transmission to higher frequencies. The relation of the magnitude of this shift to the angle of incidence for our interference filters has been experimentally determined on a Beckman IR 12. Additional data are provided by OCLI.<sup>46</sup> It then remains to calculate the amount of light as a function of the angle of incidence.

The transmission of the band  $(\nu_3) \rightarrow (\nu_3 - 1)$  through a given filter is a sum over rotational states averaged over the collection angle  $\theta$ :

$$T(f, \nu') = \int_0^{\theta_m} \rho(\theta) d\theta \left\{ \sum_J \frac{(2J+1)}{Q_R} \times \exp[-F_{\nu'}(J)/kT] [T(f, \nu_P, \theta) + T(f, \nu_R, \theta)] \right\}. \quad (14)$$

$F_{\nu'}(J)$  is the rotation energy of the upper state;  $F_{\nu'}(J) = B_{\nu'}J(J+1)$ . The function  $T(f, \nu, \theta)$  is the transmission at frequency  $\nu$  for light at an incident angle  $\theta$  through the filter  $f$ . The transition frequencies are given by

$\nu = \nu_0 + (B_v + B_v')m + (B_v - B_v')m^2$ , where  $m$  is  $(J+1)$  for an  $R$  branch ( $\nu_R$ ) but  $m$  is  $(-J)$  for a  $P$  branch ( $\nu_P$ ).  $\rho(\theta)$  is the weighting function for photons arriving at angle  $\theta$  to the normal. The exponential factor accounts for a Boltzmann distribution of rotational energy;  $Q_R$  is the rotational partition function.  $J$  varies over the rotational levels of the upper state. There are, thus, two frequencies for each  $J$ ; one for  $\Delta J = 1$  ( $\nu_R$ ) the other for  $\Delta J = -1$  ( $\nu_P$ ). For our detector  $\theta_m = 40^\circ$  (half the angle of the cone of light collected). Transmission functions for various filters and for  $\nu = 1$  to  $\nu = 4$  were calculated numerically on a small digital computer. The filters we employed, together with their bandwidths and transmission functions, are tabulated in Appendix B.

Cold gas filter experiments were run under both deactivating and nondeactivating conditions; in one instance the buffer gas in the flow tube was  $\text{H}_2$  and He but in the other only Ar. In the former case any state ( $v_1, v_2, v_3$ ) is relaxed via collisions with  $\text{H}_2$  to  $(0, 0, v_3)$ . The cold gas cell will then filter out the  $(001) \rightarrow (000)$  transition from the overtones. The ratio of intensities through the gas cell ( $I_g$ ) versus the empty gas cell ( $I_e$ ) is given by

$$\frac{I_g}{I_e} = \frac{N(002)A(2) + \dots + N(00v_3)A(v_3)}{N(001) + N(002)A(2) + \dots + N(00v_3)A(v_3)} \quad (15)$$

Under nondeactivating conditions (Ar as the buffer gas) both the numerator and denominator of Eq. (15) must include terms of the form  $N(v_1, v_2, v_3)A(v_3)$  arising from the contribution to the emission signals from combination bands. This means that the cold gas cell will be less effective as the states such as  $(011)$  will now pass through the gas cell, whereas if the bend were deactivated first, the emission would be blocked. The com-

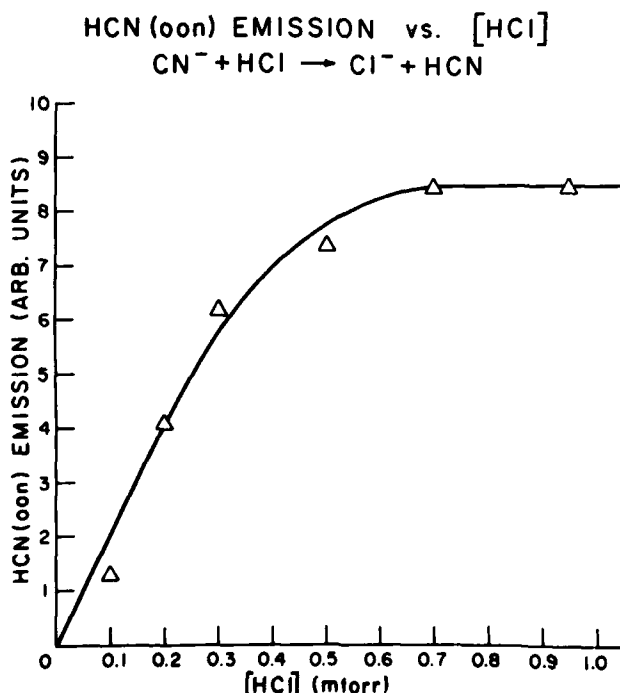


FIG. 4. Emission from the  $\nu_3$  mode of product HCN as a function of HCl pressure.

### HCN(oon) EMISSION vs. $\text{CN}^-$ $\text{CN}^- + \text{HCl} \rightarrow \text{Cl}^- + \text{HCN}$

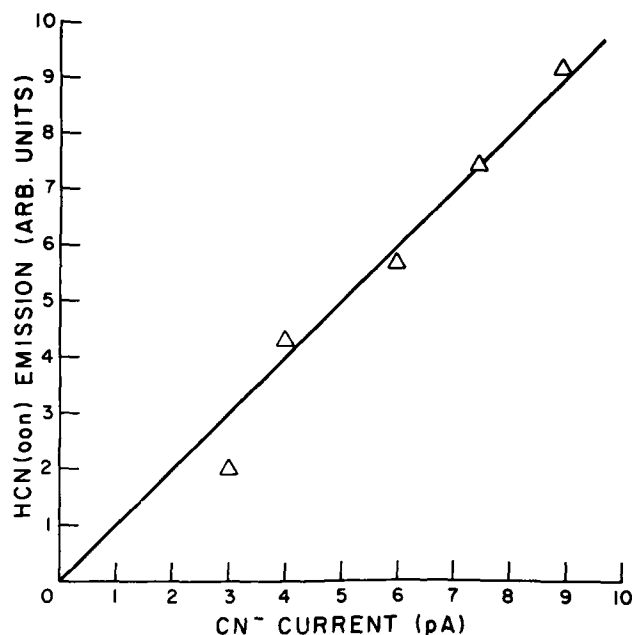


FIG. 5. HCN  $\nu_3$  emission as a function of total  $\text{CN}^-$  available for reaction.

parison of the effectiveness of the cold gas filter with and without deactivation thus gives us a measure of the amount of excitation in the bending mode.

### B. $\text{CN}^- + \text{HCl}$

We will describe in some detail the extraction of relative populations in the H-CN stretch by using Reaction (3) as an example.

Vibrational emission from the  $3300 \text{ cm}^{-1}$  region was observed when HCl was added through the neutral inlet. Several checks were made to ensure that this signal was from the ion-molecule reaction (3). One was to see that the emission intensity grew linearly with the pressure of HCl and, then, saturated as  $\text{CN}^-$  was exhausted. Figure 4 depicts this behavior. Another check revealed that the emission signal scaled linearly with the amount of  $\text{CN}^-$  generated in the presence of a saturating pressure of HCl. This is shown in Fig. 5. Possibilities of other ion reactions in the flow tube are discussed above.

The exothermicity of Reaction (3) at  $6200 \text{ cm}^{-1}$  limits the number of accessible HCN vibrational states to 92. Recall that the uncertainty in  $\Delta H_0^\circ$  is  $900 \text{ cm}^{-1}$  so this number of 92 is not precise. Note the difference as compared<sup>17</sup> to the two vibrational states available for HCl formed by  $\text{Cl}^- + \text{HI}$ . The rapid increase in numbers of states is perhaps the most prominent feature of the change from diatomic to polyatomic. CNH states are not considered for Reaction (3) as  $\text{CNH}(000)$  is just barely available with the energy released in the reaction. A simplified diagram of the  $\nu_3$  manifold for HCN

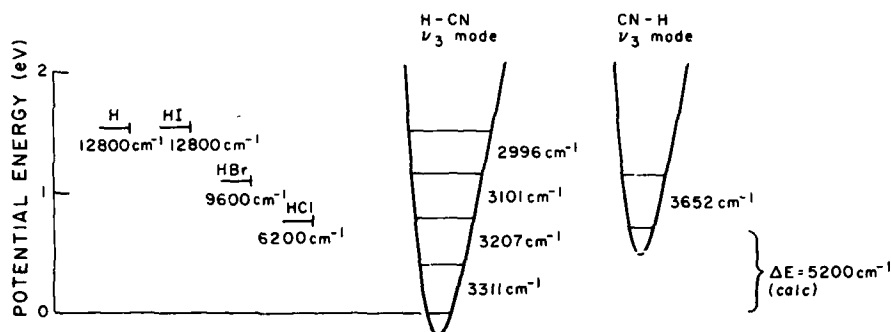


FIG. 6. Potential wells for the  $\nu_3$  mode of both HCN and CNH indicating their estimated relative stabilities. The experimentally determined vibrational splittings are indicated for both HCN and CNH. Also indicated are the exothermicities for Reactions (3)–(6).

and CNH is presented in Fig. 6. At the left of the diagram HCl is positioned  $6200\text{ cm}^{-1}$  above  $v=0$  of HCN. The  $900\text{ cm}^{-1}$  error bars are indicated in Fig. 6 which suggest that there is some chance to produce  $\text{HCN}(00^02)$ .

The large number of available states reflects the various levels of excitation in the bending manifold. These can be eliminated by deactivation by addition of  $\text{H}_2$  to the flow tube. With  $\nu_2$  now 0, six states then remain:  $(00^00)$ ,  $(00^01)$ ,  $(00^02)$ ,  $(10^00)$ ,  $(20^00)$ , and  $(10^01)$ . Collision with the buffer gas reaction (9) may equilibrate the  $\text{C}\equiv\text{N}$  stretch with the bend manifold so that  $\text{H}_2$  collisions should also remove any excitation in  $\nu_1$ . Only three states now remain:  $\nu_3=0, 1$ , or  $2$ . We have no direct measure of the population of HCN with  $\nu_3=0$ . The cold gas filter gives the ratio  $I_e/I_0=0.19\pm0.02$ . Inverting Eq. (15), which now contains only two terms, we have

$$\frac{N(002)}{N(001)} = \frac{I_e/I_0}{[1 - (I_e/I_0)]A(2)} \quad (16)$$

This produces a population ratio  $N(002)/N(001)$  of  $0.11\pm0.03$ .

As mentioned earlier, there is a correction to this ratio due to the deactivation of the C–H stretch by He and  $\text{H}_2$ . Additionally, a correction should be considered for the loss of energy from the  $\nu_3$  mode by radiative cascading. Both of these can be combined into

$$\frac{d}{dt} \mathbf{N}_t = \Gamma \mathbf{N}_t, \quad (17)$$

where  $\mathbf{N}_t = [N(2), N(1), N(0)]_t$ , the vector of fractions of HCN with  $\nu_3=0, 1$ , or  $2$  at time  $t$ . The solution is

$$\mathbf{N}_t = \mathbf{N}_0 \exp(\Gamma t), \quad (18)$$

which can be inverted to recover the population at time  $t=0$  from that at time  $t$ .  $\Gamma$  is the relaxation matrix

$$\Gamma = \begin{pmatrix} -A_{002} - k_{002}[\text{H}_2] & 0 & 0 \\ A_{002} + k_{002}[\text{H}_2] & -A_{001} - k_{001}[\text{H}_2] & 0 \\ 0 & A_{001} + k_{001}[\text{H}_2] & 0 \end{pmatrix} \quad (19)$$

$A_{00\nu_3}$  is the spontaneous emission rate and  $k_{00\nu_3}$  is the deactivation rate constant for  $(00r_3) \rightarrow (0, 0, r_3-1)$ . Inserting the observed<sup>18</sup> Einstein coefficient  $A_{001}=74.1\text{ sec}^{-1}$ ,  $k_{001}=200\text{ Torr}^{-1}\text{ sec}^{-1}$ ,  $[\text{H}_2]=0.5\text{ Torr}$  and  $t=0.6\text{ msec}$ , with  $A_{002}=2A_{001}$  and  $k_{002}=2k_{001}$  (assuming the harmonic oscillator approximation) gives the corrected value  $N(002)/N(001)=0.12\pm0.03$ . As expected, the correc-

tion is on the order of 10%. It is also within the error bounds of the measurements.

Although the relative amounts of  $\nu_3=1$  and  $\nu_3=2$  can be determined, the probabilities remain unknown as long as no information on the level with  $\nu_3=0$  exists. In order to determine some limits for the probabilities, the total emission signal from HCN produced by  $\text{CN}^- + \text{HCl}$  was compared to the total emission signal from HCl formed by the reaction  $\text{Cl}^- + \text{HBr}$ . This was accomplished by changing only the precursor and adjusting the emission current such that the same ion current could be measured at the Faraday plate for each ion. The ratio of total emission from these two sources was 1.

We can write this ratio of intensities as

$$\frac{I(\text{CN}^- + \text{HCl})}{I(\text{Cl}^- + \text{HBr})} = \frac{N(001)A(001) + N(002)A(002)}{N(1)A(1)} \quad (20)$$

or

$$= \left\{ \frac{P(1, \text{CN}^- + \text{HCl}) + P(2, \text{CN}^- + \text{HCl})[A(002)/A(001)]}{P(1, \text{Cl}^- + \text{HBr})} \right\} \times \frac{A(001)}{A(1)}$$

Here,  $P(1, \text{CN}^- + \text{HCl})$  is the probability of forming HCN with  $\nu_3=1$ . Employment of  $A(001)=74.1\text{ sec}^{-1}$  for HCN and  $A(1)=34.6\text{ sec}^{-1}$  for HCl, produces a ratio of 2.14 for the Einstein coefficients. Using  $A(002)/A(001)=2$  and inserting  $P(2, \text{CN}^- + \text{HCl})=0.12 P(1, \text{CN}^- + \text{HCl})$ , we obtain

$$\frac{P(1, \text{CN}^- + \text{HCl})}{P(1, \text{Cl}^- + \text{HBr})} = 0.37 \quad (21)$$

The reactions of chloride ions with HBr and HI have been studied earlier in this apparatus.<sup>17</sup> In a manner analogous to Eq. (20),  $P(1, \text{Cl}^- + \text{HBr})/P(1, \text{Cl}^- + \text{HI})$  was found to be 0.96.  $P(1, \text{Cl}^- + \text{HBr})$  is the probability of forming  $\text{HCl}(v=1)$  by the reaction of  $\text{Cl}^-$  with HBr. From an extrapolation of a surprisal plot, the probabilities  $P(0, \text{Cl}^- + \text{HI})=0.21$ ,  $P(1, \text{Cl}^- + \text{HI})=0.43$  and  $P(2, \text{Cl}^- + \text{HI})=0.36$  were obtained. This set of probabilities implies  $P(1, \text{Cl}^- + \text{HBr})=0.41$ . As an extreme case, we could ignore the surprisal analysis and choose  $(0, 0.54, 0.46)$  as the vibrational distribution of HCl formed from  $\text{Cl}^- + \text{HI}$  rather than  $(0.21, 0.43, 0.36)$ . This produces an upper limit for  $P(1, \text{Cl}^- + \text{HBr})$  of 0.52.

This indicates an uncertainty in our probabilities of  $\pm 25\%$ .

We can now use these earlier  $\text{Cl}^-$  results to interpret our  $\text{CN}^-$  reactions. If the surprisal value is retained for  $P(1, \text{Cl}^- + \text{HBr})$ , we use Eq. (21) to find  $P(1, \text{CN}^- + \text{HCl}) = 0.15$ . The complete distribution is then  $P(0, \text{CN}^- + \text{HCl}) = 0.83$ ,  $P(1, \text{CN}^- + \text{HCl}) = 0.15$  and  $P(2, \text{CN}^- + \text{HCl}) = 0.02$ . These results are prone to error from the measured ratio of total intensities, the neglect of  $\text{CNH}(000)$ , and from the earlier analysis of the  $\text{Cl}^-$  reactions. A reasonable error to assign those probabilities is  $\pm 25\%$ .

Experiments with argon as the carrier gas were also undertaken. They resulted in a change of the ratio of intensities with and without the cold gas cell to  $I_e/I_e = 0.8 \pm 0.1$ . The increase from the previous value of 0.19 implies that the HCN molecules with  $\nu_3 = 1$  are usually accompanied with excitation in the bending mode. Instead of Eq. (15), a more complicated expression must be used for the intensity ratio

$$\frac{I_e}{I_e} = \frac{A(002)N(002) + \Sigma A(0k1)N(0k1)}{A(001)N(001) + A(002)N(002) + \Sigma A(0k1)N(0k1)}$$

We conjecture that the spontaneous emission coefficient is the same for  $(0k1) \rightarrow (0k0)$  as for  $(001) \rightarrow (000)$ . If  $\Sigma N(0k1)$  is referred to as  $N(0n1)$ , we have

$$\frac{N(0n1)}{N(001)} = \left[ \frac{N(002)}{N(001)} \left( \frac{I_e}{I_e} - 1.0 \right) A(2) + \frac{I_e}{I_e} \right] \left( 1.0 - \frac{I_e}{I_e} \right)^{-1} \quad (22)$$

Inserting the value  $N(002)/N(001) = 0.12$  we see that  $N(0n1)/N(001) = 4 \pm 2$ . This is rather interesting: 4/5 of the HCN formed with one quantum in  $\nu_3$  also have at least one quantum in  $\nu_2$ . It seems quite likely then that a similar fraction of HCN with  $\nu_3 = 0$  would also have  $\nu_2 > 0$ . In other words, about 80% of the HCN formed by  $\text{CN}^- + \text{HCl}$  will have some excitation in the bending mode.

### C. Relaxation of $\text{HCN}(0n0)$

While dealing with Reaction (3), a discussion of the relaxation of  $\text{HCN}(0n0)$  is in order. It is useful to compare the relaxation properties of HCN to another triatomic molecule about which a great deal is known,  $\text{CO}_2$ .

Measurements of  $I_e/I_e$  were made at distances of 11 and 5 cm from the neutral inlet to the IR detector with  $\text{H}_2 + \text{He}$ ,  $\text{He}$ , and  $\text{Ar}$  as the carrier gas. A value of  $I_e/I_e = 0.8 \pm 0.1$  was obtained at each distance when the collision partner was argon. This allows an upper bound for the rate constant to be obtained by assuming that the maximum fraction deactivated is given by 0.7/0.9 (the worst case within the error limits). With  $t = 1.0$  ms and  $\text{Ar} = 0.3$  Torr, the upper limit for the rate constant [Eq. (10) with  $M = \text{Ar}$ ] is  $k_{\text{Ar}} < 1000 \text{ Torr}^{-1} \text{ sec}^{-1}$  at  $T = 295$  K. This may be compared to the value of  $k_{010}$  for  $\text{CO}_2 = 26 \text{ Torr}^{-1} \text{ sec}^{-1}$ .<sup>42</sup>

At the other extreme, with the carrier gas a mixture of 0.1 Torr  $\text{H}_2$  and 0.4 Torr  $\text{He}$ ,  $I_e/I_e = 0.19 \pm 0.02$  at each distance. Thus, all of the energy in the bending mode has been removed in 0.6 msec. This time a lower limit of the rate constant can be obtained [Eq. (10) with

$M = \text{H}_2$ ]. Assuming that, with the 11 cm distance, 95% of the bending mode has been deactivated yields  $k_{\text{H}_2} > 2 \times 10^4 \text{ Torr}^{-1} \text{ sec}^{-1}$ ; compare with  $k_{010} = 4 \times 10^4 \text{ Torr}^{-1} \text{ sec}^{-1}$  for the (VT) deactivation of  $\text{CO}_2(01^10)$  by hydrogen.<sup>42,43</sup>

Helium deactivates  $\text{HCN}(0n1)$  at a rate intermediate to these two. The intensity ratios through the cold gas filter were as follows: for 0.5 Torr  $\text{He}$   $I_e/I_e = 0.25 \pm 0.02$  at 11 cm,  $0.37 \pm 0.04$  at 5 cm and for 0.27 Torr  $I_e/I_e = 0.26 \pm 0.04$  at 11 cm,  $0.57 \pm 0.05$  at 5 cm. Note that the values at 11 cm are reasonably close to 0.19. In fact, were they used in Eq. (15), the results would be  $N(2)/N(1) = 0.17$  and  $N(2)/N(1) = 0.18$ , respectively; not very different from the actual value. The values obtained at 5 cm are treated as described for the argon case. Equation (22) is used giving  $N(0n1)/N(001) = 0.35 \pm 0.1$  for 0.5 Torr  $\text{He}$  and  $N(0n1)/N(001) = 1.1 \pm 0.3$  for 0.27 Torr  $\text{He}$ . The rate constant can then be extracted from

$$\ln \left[ \frac{N(0n1)/N(001) \text{ in He}}{N(0n1)/N(001) \text{ in Ar}} \right] = -k[\text{He}]t$$

At both helium pressures the result is within the error bounds of  $k_{\text{He}} = 7 \pm 4 \times 10^3 \text{ Torr}^{-1} \text{ sec}^{-1}$ . The corresponding deactivation rate for  $\text{CO}_2$  is  $k_{010} = 3.5 \times 10^3 \text{ Torr}^{-1} \text{ sec}^{-1}$ .<sup>42</sup> Hence, while the results for HCN are approximate, they are in keeping with the prediction that  $\text{CO}_2$  would be useful as a guide.

### D. $\text{CN}^- + \text{HBr}$

Owing to the larger exothermicity of the reaction, the maximum quantum number for the C-H stretch is  $\nu_3 = 3$ , 14 for the bending mode, and 4 for the  $\text{C} \equiv \text{N}$  stretch; the total number of states is 344. Note also Fig. 6. In the hydrogen-helium gas mixture the ratio  $I_e/I_e = 0.65 \pm 0.05$  is measured with the cold gas filter. Substituted into Expression (15), this gives  $N(002)/N(001) = 1.1 \pm 0.1$ . This is not quite correct as excitation to  $\nu_3 = 3$  is just possible. To check for this, fixed frequency filters were used with the results shown in Appendix B. After the deconvolution procedure discussed above, these results combined with the cold gas filter results yield the ratios  $[N(001):N(002):N(003)] = [0.51:0.44:0.05]$ . Errors for these values are  $\pm 10\%$ . From this we see that when the extra energy is available, the population of  $\nu_3 = 2$  is just as likely as for  $\nu_3 = 1$ . It is interesting to note that, as in the  $\text{HCl}$  reaction, a small fraction of the HCN is formed with practically all of the exothermicity contained in the newly formed C-H bond.

The cold gas filter has almost no effect when the reaction is run in argon. A ratio of  $I_e/I_e = 0.95 \pm 0.05$  is measured. Equation (22) then gives  $N(0n1)/N(001) = 13 \pm 10$ , the large error resulting from the denominator being close to zero in Eq. (22). This shows that even more so than for the  $\text{HCl}$  reaction, the majority of the product HCN is born with some excitation in the bending mode.

### E. $\text{CN}^- + \text{HI}$

The larger exothermicity of  $12800 \text{ cm}^{-1}$  drastically increases the number of available states in the product

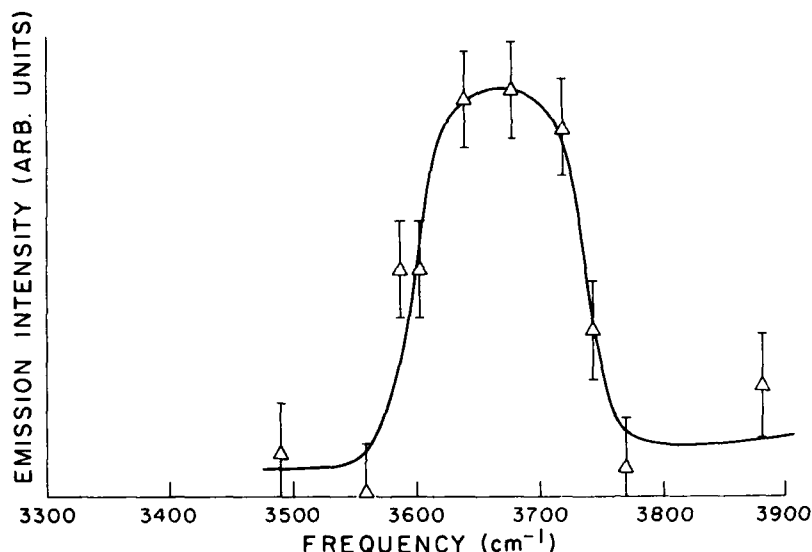
OBSERVED HIGH FREQUENCY EMISSION  
FROM REACTION:  $\text{CN}^- + \text{HI}$ 

FIG. 7. The results of a point-by-point scan through the high frequency emission spectrum seen in Reaction (5), confirming the assignment as  $\text{CNH}(\nu_1)$  emission.

$\text{HCN}$ . Roughly 880 vibrational states are accessible. In addition to excitation of  $\text{HCN}$ , reference to Fig. 6 suggests to us that excited states of  $\text{CNH}$  may be produced as well. The difference between the zero point energies of those isomers is not certain but, as mentioned above, several computations estimate it at about  $5200\text{ cm}^{-1}$ . This implies that about  $7600\text{ cm}^{-1}$  are available for excitation of  $\text{CNH}$ . Under conditions where  $\nu_1$  and  $\nu_2$  are deactivated, only five states of  $\text{HCN}$  are left: (000), (001), (002), (003), and (004). Based on the zero point separation of  $\text{CNH}$  from  $\text{HCN}$  ( $\Delta E$  in Fig. 6), (001) and (002) of  $\text{CNH}$  must be considered for Reaction (5).

The first experiments with  $\text{HI}$  gave strong evidence for the presence of  $\text{CNH}$  as a reaction product. When  $\text{CN}^-$  is mixed with  $\text{HI}$  in the flow tube, very strong emission is observed when filter WO2644 (see Appendix B) is used. Much weaker signals are found when filter Type 1#4 is employed. Appendix B reports that the latter signal is only about 30% of the former. Appendix B indicates that the essential difference between the filters is that WO2644 transmits light from 3270 up to about  $4500\text{ cm}^{-1}$ . It is strongly suggested that we are producing molecules which have high frequency modes emitting in the range 3400 to  $4500\text{ cm}^{-1}$ . Very few  $\text{C-H}$  stretches occur at such high frequencies. The possibility of emission from an  $\text{O-H}$  stretch (in  $\text{H}_2\text{O}$  or some alcohol) can be dismissed since there is no reason why such a mechanism would occur with only the  $\text{HI}$  reaction.  $\text{HCN}$  has no excited electronic states accessible at these energies. The cyano radical  $\text{CN}$  does have a low lying  $^2\Pi$  state,<sup>30</sup> but it is endothermic to form it as a product in these ion reactions. If  $\text{CN}(^2\Pi)$  were formed by detachment of  $\text{CN}^-$  at the ion shutter, then the emission would be present for all the reactions. These high frequency signals are observed when either  $\text{BrCN}$  or  $\text{C}_2\text{N}_2$  is the  $\text{CN}^-$  precursor.

We believe that this high frequency emission is from

vibrationally excited  $\text{CNH}$ . Table III indicates that the  $\text{N-H}$  stretch is at  $3652.9\text{ cm}^{-1}$ . A frequency such as this is entirely consistent with our observations. Two further experiments establish  $\text{CNH}$  as the carrier of this signal. The first is the direct observation of hydroisocyanic acid with a  $\text{Ge:Cu}$  IR detector. The second experiment is the direct observation of emission of  $\text{CND}$  when  $\text{CN}^-$  is added to  $\text{DI}$ .

We can replace our  $\text{InSb}$  detector and its fixed frequency filter with a background limited  $\text{Ge:Cu}$  detector. This device is housed in a liquid helium Dewar and configured with wavelength selective circular variable interference filters. The high frequency radiation produced by  $\text{CN}^-$  and  $\text{HI}$  was monitored with this scanning detector and the resulting emission spectrum is shown in Fig. 7. The peak in the chemiluminescent signal is about  $3650\text{ cm}^{-1}$ —precisely the frequency of  $\text{CNH}(001)-(000)$ . Even though the resolution of the circular variable filters is about  $80\text{ cm}^{-1}$ , this signal is easily separated and distinct from the region of  $\nu_3$  emission of  $\text{HCN}$  ( $3300\text{--}2900\text{ cm}^{-1}$ ).

If  $\text{CNH}$  is being produced, we should observe an isotope effect. Table III indicates that the (001)-(000) transition of  $\text{DCN}$  is at  $2630\text{ cm}^{-1}$  but is shifted in  $\text{CND}$  to  $2780\text{ cm}^{-1}$ . We have experimentally observed this shift. If we add  $\text{CN}^-$  to  $\text{DI}$  in the flow tube and search for emission with an  $\text{InSb}$  detector and the fixed frequency filter NO3462 (bandpass  $2984\text{--}2799\text{ cm}^{-1}$ ), we see a signal. This is shown in Fig. 8. Notice that this filter will completely block all signals from  $\text{DCN}$ . Figure 8 clearly shows emission from the  $\text{CN}^- + \text{DI}$  reaction. This is consistent with the isotope shift predicted for  $\text{CND}$ . There are at least two reasons why the signal in Fig. 8 is so weak. The first is that our filter NO3462 only transmits a fraction of the  $R$  branch of the band. An additional factor is the decrease in the Einstein  $A$  factor of  $\text{CNH}$  upon isotopic substitution. The ratio of

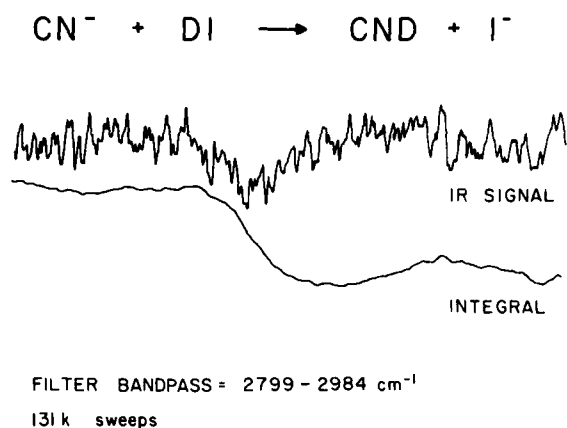


FIG. 8. Emission signal from CND ( $\nu_3$ ) following 10 min of signal averaging.

the  $A$  factor for CND to that for CNH should be about  $(2780/3652)^3$  or 0.4. Both the frequency and intensity of the signal shown in Fig. 8 are consistent with CND emission.

Measurements of the intensities of emission signals were made with a cold gas filter and four fixed frequency filters; the results are collected in Appendix B. Even with  $\text{H}_2$  to deactivate the bends, the cold gas filter ratio was high:  $I_g/I_e = 0.9 \pm 0.06$ . Part of the reason for this may lie with the possibility of putting up to 19 quanta into  $\nu_2$ , with  $\text{H}_2$  unable to complete the sequential processes such as  $(0, 18, 0) + \text{H}_2 \rightarrow (0, 17, 0) + \text{H}_2$ , etc., in the time available. To invert the observed intensities from  $\text{CN}^- + \text{HI}$  listed in Appendix B, we use our estimate that  $A_{\text{CNH}}$  is about four times greater than  $A_{\text{HCN}}$ . An additional, necessary datum is that  $T(\text{WO2644}, \text{CNH}) = 0.73$ . We find the following relative populations for the HI reaction:

$$[N(--1): N(--2): N(--3): N(--4): N(\text{CNH})] \\ = [0.21: 0.47: 0.11: 0.02: 0.19].$$

Partly due to the sensitivity of the numbers on the cold gas filter ratio, the error bounds are given as  $\pm 40\%$ .

#### F. $\text{CN}^- + \text{H}$

Reaction (6) has been studied before.<sup>47</sup> The exothermicity for this reaction is roughly the same as for  $\text{CN}^- + \text{HI}$ . Consequently about the same number of states are available to the reaction products as in the previous section. Surprisingly enough, we find no evidence for vibrationally excited CNH as a reaction product of this associative detachment reaction. The intensity ratios for a set of filters are reported in Appendix B. A deconvolution of these fixed frequency filters and cold gas cell results gave the relative populations

$$[N(--1): N(--2): N(--3): N(--4)] \\ = [0.47: 0.39: 0.09: 0.05].$$

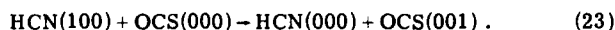
As in the HI reaction, the error bars are large and on the order of  $\pm 30\%$ .

Attempts to determine the excitation in the bending manifold by running the experiment in argon did not give satisfactory results. The main problems stemmed from the lack of knowledge about the amount of  $\text{H}_2$  entering the flow tube through the atom generator and of the deactivation rate of HCN by hydrogen atoms.

#### G. Energy transfer to OCS

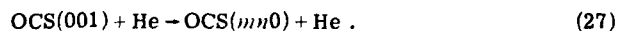
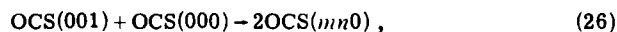
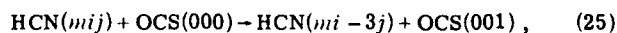
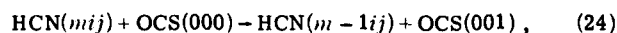
An unknown in these experiments is the state of the  $\text{C}\equiv\text{N}$  stretch  $\nu_1$  in the product HCN. Since emission from this mode is nil, we have no chance to observe it in fluorescence. Dark modes such as this may be commonly encountered as we study more complicated polyatomic molecules. We need another avenue to detect weak modes. One possible method is to collisionally transfer energy to a bright emitter, as for example in Reaction (23), where OCS is used as an acceptor.

The idea is this:



OCS was chosen for several reasons. The asymmetric stretch of OCS is at  $\nu_3 = 2062.2 \text{ cm}^{-1}$ ; this is only  $34 \text{ cm}^{-1}$  below the  $(100) \rightarrow (000)$  transition frequency in HCN. The small energy defect makes it likely that the rate constant for energy transfer from HCN to carbonyl sulfide will be quite fast. The rate constant<sup>48</sup> for  $V \rightarrow V$  transfer from  $\text{CO}(v=1)$  to  $\text{OCS}(001)$  is  $2.57 \times 10^5 \text{ Torr}^{-1} \text{ s}^{-1}$  at 300 K. Energy equilibration in vibrationally excited OCS has been thoroughly studied.<sup>49,50</sup> In order to accomplish the transfer from HCN in the 1 ms our flow tube allows, a  $V \rightarrow V$  rate constant of roughly  $k_{23} = 5 \times 10^3 \text{ Torr}^{-1} \text{ sec}^{-1}$  or greater is required. OCS is an extremely bright emitter ( $S_3 = 2634 \text{ atm}^{-1} \text{ cm}^{-2}$ ) so even if a fraction of the energy is transferred, emission should be observed from the OCS.

The following reactions are important in this scheme:



Collisional equilibration as in Eq. (9) is crucial to this discussion. As already stated,  $k_{24}$  should be large. Because the energy defect is also small for Reaction (25),  $38 \text{ cm}^{-1}$ , this too might be rapid. Hence, it will not be possible to determine whether the energy transferred to the OCS originated from the  $\text{C}\equiv\text{N}$  stretch or from the bending mode. The rate constant for the self-relaxation of OCS has been measured<sup>48</sup> and is fast;  $k_{26} = 4.7 \times 10^4 \text{ Torr}^{-1} \text{ sec}^{-1}$ . This limits the amount of OCS which can be added to the flow tube to about 10 mTorr. At this pressure 35% of the energy placed into OCS will be deactivated by Reaction (26) by the time the molecules reach the detector. Hancock *et al.*<sup>48</sup> have measured the rate constant for deactivation of OCS by Ar to be  $1.4 \times 10^3 \text{ Torr}^{-1} \text{ sec}^{-1}$ . If we assume the same rate constant as for He, this means that 50% of the  $\text{OCS}(001)$  will have been lost due to helium collision before detection.

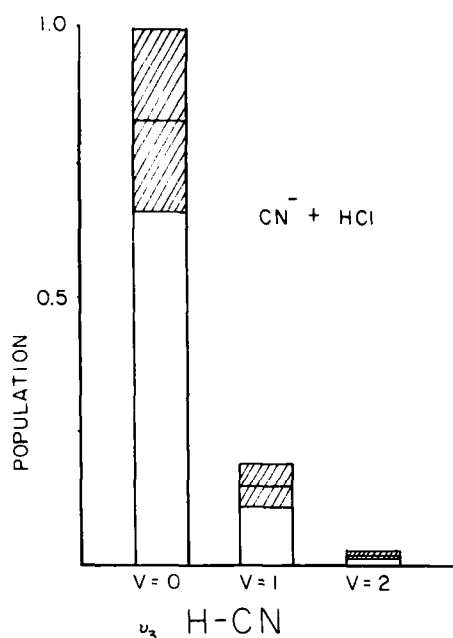
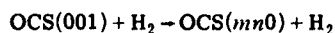


FIG. 9. A histogram of the product distribution for the  $\nu_3$  mode of HCN produced by Reaction (3). The hatched areas indicate the error bars.

Even though the rate constants  $k_{24}$  and  $k_{25}$  were unknown and though  $\frac{3}{4}$  of the OCS would be deactivated before we had a chance to observe emission, the experiment was tried.  $\text{CN}^-$  and  $\text{HBr}$  alone were combined in the flow tube in view of a filter which accepted light from both  $\text{HCN}(100)$  and  $\text{OCS}(001)$ . No emission was observed. Addition of 10 mTorr of OCS 10 cm upstream from the InSb detector led to a moderate amount of IR emission. Use of a cold gas cell filled with 25 Torr of OCS blocked emission completely, demonstrating that the emitter is  $\text{OCS}(001)$ . If  $\text{CN}^-$  is added to the flow tube together with OCS but no  $\text{HBr}$ , no IR emission is seen. By varying the  $\text{H}_2$  pressure in the buffer gas from 0 to 150 mTorr, we can make a crude estimate of  $1 \times 10^4 \text{ Torr}^{-1} \text{ sec}^{-1}$  for the rate constant of the quenching Reaction (12). These experiments prove that we can collisionally transfer energy from the product HCN to OCS and detect it.

Is the energy transfer specific? Can we prove that the donating species is  $\text{HCN}(100)$  and not  $\text{HCN}(030)$ ? The answer is that our results are ambiguous; these transfer experiments cannot distinguish donation by  $\text{HCN } \nu_1$  from  $\text{HCN } 3\nu_2$ . We cannot be sure if Eq. (9) equilibrates the manifolds or not.

If we add 10 mTorr  $\text{H}_2$  to the  $\text{CN}^- + \text{HBr}$  reaction zone 10 cm upstream from OCS addition, all OCS emission is quenched. Now the process



has a measured<sup>51</sup> collision number of 126 000. It is evident that  $\text{H}_2$  is not relaxing the  $\text{OCS}(001)$ , but is quenching the vibrationally excited HCN formed by the reaction. Consequently it appears that if Eq. (9) equilibrates  $\nu_1$  with  $\nu_2$ , both modes are relaxed by the  $\text{H}_2$ . If Eq. (9) does not equilibrate the modes, then no  $\text{HCN}(v-v)$  is a reaction product.

## V. DISCUSSION

The major fact to emerge from this work is that it has been possible to study the energy distribution in a polyatomic molecule born in an ion-molecule reaction. It is apparent that the excess vibrational energy does not become scrambled among the available vibrational modes while the reactants pass through the deep potential well separating reactants and products. We have been able to derive information on the degree of excitation of the product HCN in the  $\nu_3$  manifold. Unfortunately, we can say very little about the energy distribution in the other modes except that a considerable number of bending quanta must be excited ( $\nu_2$ ).

A comparison between the total IR intensity emitted by the reactions  $\text{CN}^- + \text{HCl}$  and  $\text{Cl}^- + \text{HX}$  has demonstrated that a high fraction of the HCN is produced in the ( $\nu_3 = 0$ ) state (see Sec. IV B). A histogram of this nascent distribution is shown in Fig. 9. This analysis does not depend upon the accuracy of a surprisal plot based on a very limited amount of data. Table IV collects the relative product HCN distributions resulting from the  $\text{CN}^- + (\text{HCl}, \text{HBr}, \text{HI}, \text{and } \text{H})$  reactions. These are the nascent distributions for the C-H stretching mode  $\nu_3$ . A histogram of these data is presented in Fig. 10. Naturally, we have no direct measure of the  $\nu_3 = 0$  population. As one goes from the case of  $\text{HCl}$ , to  $\text{HBr}$ , to  $\text{HI}$  and  $\text{H}$ , the reactions become more exothermic (see Table I) and the product distributions become hotter. As remarked earlier, each reaction produces some fraction of the HCN product molecules excited to the highest level in the  $\nu_3$  ladder which is energetically accessible. It is apparent that the vibrational energy distribution in the HCN is not random.

In the previous studies of  $\text{Cl}^-$  or  $\text{F}^-$  dynamics,<sup>17,52,53</sup> angular momentum restrictions markedly affected the distributions in the associative detachment reactions  $\text{Cl}^- + \text{H} \rightarrow \text{HCl}(v)$  or  $\text{HF}(v) + e^-$ . In both cases, most of the angular momentum associated with the in-

TABLE IV. Relative product distributions for  $\text{CN}^-$  reactions.

Reaction	H-CN ( $\nu_3$ )			P (4)	CN-H ( $\nu_3$ )
	P (1)	P (2)	P (3)		P (1)
$\text{CN}^- + \text{HCl}$	$0.89 \pm 0.03$	$0.11 \pm 0.03$	...	...	...
$\text{CN}^- + \text{HBr}$	$0.51 \pm 0.05$	$0.44 \pm 0.05$	$0.05 \pm 0.02$	...	...
$\text{CN}^- + \text{HI}$	$0.21 \pm 0.10$	$0.47 \pm 0.13$	$0.11 \pm 0.06$	$0.02 \pm 0.02$	$0.19 \pm 0.05$
$\text{CN}^- + \text{H}$	$0.47 \pm 0.05$	$0.39 \pm 0.10$	$0.09 \pm 0.04$	$0.05 \pm 0.03$	$0.0 \pm 0.05$

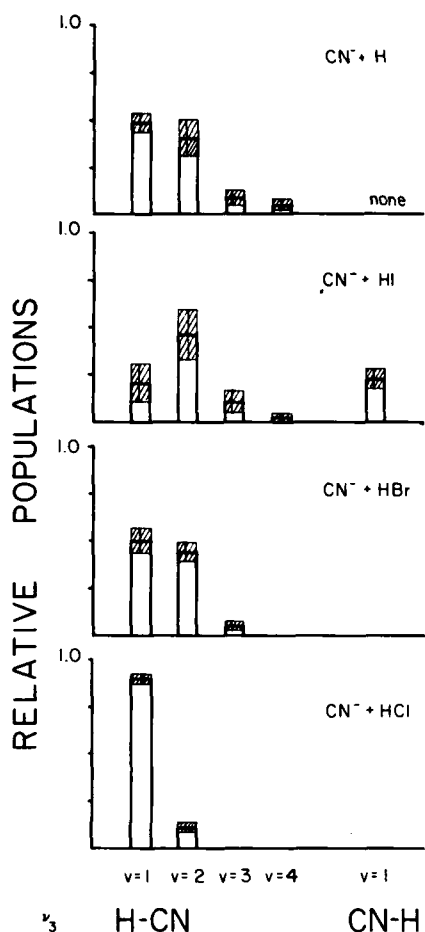


FIG. 10. A histogram of the observed product distributions (Table IV) for the  $\nu_3$  modes of HCN and CNH in Reactions (3)–(6). The hatched areas are indications of the errors in these distributions. Each distribution is normalized to 1.0 ignoring population in the  $\nu=0$  states.

coming particles was lodged in the product  $\text{HX}$  molecules as rotation. The large rotational spacings<sup>30</sup> for  $\text{HF}$  and  $\text{HCl}$  require that this obligatory rotational energy is a significant portion of the reaction energy available. In both reactions, the vibrational energy distributions of the product  $\text{HF}$  and  $\text{HCl}$  molecules manifest a noticeable truncation of the higher  $\nu$ 's excited.

Both  $\text{HCl}$  and  $\text{HF}$  are unusual molecules with large rotational constants.<sup>30</sup>  $\text{HCN}$  is more typical with a  $B_r$  of about  $1.5 \text{ cm}^{-1}$  (Table III). Consequently, in Reaction (6), angular momentum restrictions require only roughly  $275 \text{ cm}^{-1}$  of energy to be placed in rotation. This is a rather small portion of the total energy available to  $\text{HCN}$  ( $12\,800 \text{ cm}^{-1}$ ), so there is no distortion of the product vibrational distribution.

A second important and unexpected result of these studies is the detection of  $\text{CNH}$ , produced in the reaction of  $\text{CN}^-$  with  $\text{HI}$ . In fact,  $\text{CNH}$  represents roughly 20% of the excited product molecules formed in Reaction (5).

As implied in Fig. 10, our experiments allow us to

place bounds on the zero point energy difference between  $\text{HCN}$  and  $\text{CNH}$  (shown in Fig. 6 as  $\Delta E$ ). Since we observe vibrationally excited  $\text{CNH}$  as a reaction product from  $\text{CN}^- + \text{HI}$  but not from  $\text{CN}^- + \text{HBr}$ ,  $\Delta E$  must be less than  $9200 \text{ cm}^{-1}$ . This number is based on the reaction exothermicity of Reaction (5) and the  $3600 \text{ cm}^{-1}$  necessary to excite  $\text{CNH}$  from (000) to (001). In contrast, Reaction (4) does not seem to be exoergic enough to generate  $\text{CNH}$  ( $\nu_3=1$ ); so  $\Delta E$  is probably greater than  $6000 \text{ cm}^{-1}$ . Our conjecture is, then,  $6000 \text{ cm}^{-1} < \Delta E < 9200 \text{ cm}^{-1}$ . The only other value reported<sup>34</sup> for  $\Delta E$  is  $3670 \text{ cm}^{-1}$ , much lower than our estimate. However, our bounds are in reasonable agreement with *ab initio* theoretical values<sup>32,33</sup> for  $\Delta E$  of about  $5200 \text{ cm}^{-1}$ .

The rearrangement or isomerization of  $\text{CNH}$  to  $\text{HCN}$  has been the subject for a great deal of theoretical study. Many groups have computed potential surfaces for these isomeric species<sup>32,33,54</sup> and several trajectory studies<sup>55</sup> have been made of the isomerization dynamics. Another unlikely fact to emerge from our experiments is that  $\text{HCN}(\nu=4)$  does not equilibrate with  $\text{CNH}$ . Table IV and Fig. 10 report that  $\text{HCN}(\nu=4)$  is produced by  $\text{CN}^- + \text{H}$ , Reaction (6). Once  $\text{HCN}$  is born with  $\nu=4$ , it remains in the  $\text{HCN}$  well; no excited  $\text{CNH}$  is detected. This suggests that the barrier separating  $\text{CNH}$  from  $\text{HCN}$  is greater than  $6600 \text{ cm}^{-1}$ . This value comes from our minimum  $\Delta E$  ( $6000 \text{ cm}^{-1}$ ) and the energy of  $\text{HCN}$  (004) ( $12\,600 \text{ cm}^{-1}$ ). A barrier height of about  $10\,500 \text{ cm}^{-1}$  has been theoretically calculated for this separation.<sup>32,33</sup> This value is consistent with our observations.

The formation of  $\text{CNH}$ , an interstellar molecule, by a negative ion-molecule reaction is most provocative. As mentioned earlier, hydroisocyanic acid has been observed in the Orion Nebula by radio emission.<sup>22,56–58</sup> Several of the postulated schemes to synthesize  $\text{CNH}$  in outer space are based on positive ion reactions.<sup>59</sup> No proposals for  $\text{CNH}$  production based on negative ions have yet been made. Although we now have a proven case for  $\text{CN}^-$  as a  $\text{CNH}$  precursor, our only example involves  $\text{HI}$ . For  $\text{CN}^-$  to be implicated in interstellar  $\text{CNH}$  production, Reaction (6) with hydrogen atoms may be decisive. We find no evidence that Reaction (6) produces  $\text{CNH}$ , even though it is certainly exothermic enough to do so (Table I). Conceivably, Reaction (6) could yield  $\text{CNH}(\nu=0)$ , but it seems unlikely to us that there would be absolutely no accompanying  $\text{CNH}(\nu=1)$ . If  $\text{CN}^-$  is to react with something in the interstellar medium to produce  $\text{CNH}$ ,  $\text{H}$  is the best bet, not  $\text{HI}$ .<sup>58</sup> It appears that reactions of  $\text{CN}^-$  probably are not important in the synthesis of astrophysical  $\text{CNH}$ .<sup>60</sup>

The reason for the failure of  $\text{CN}^- + \text{H}$  to yield  $\text{CNH}(\nu)$  is not clear. Since we see emission from  $\text{HCN}(\nu=4)$ , we know that Reaction (6) has enough energy to form both isomers. One speculative mechanism that may account for the lack of  $\text{CNH}(\nu)$  production in Reaction (6) can be borrowed from Fehsenfeld<sup>47</sup> and is shown in Fig. 11. We could imagine that  $\text{CN}^- + \text{H}$  may form a negative ion ( $\text{HCN})^-$  which is stable enough to enter the autodetaching region (curve II in Fig. 11). On the other hand, if  $\text{CN}^- + \text{H}$  forms the isomeric ion ( $\text{CNH})^-$  it may not be stable enough to enter the autodetaching

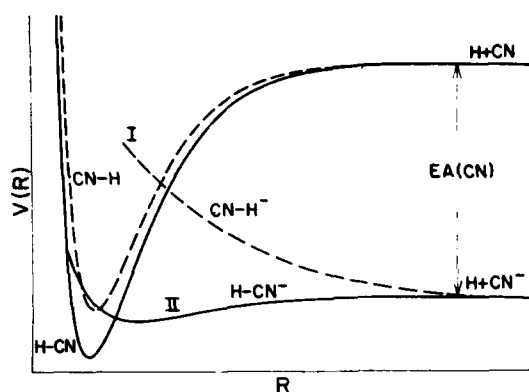


FIG. 11. A conjectured set of potential curves to describe the associative detachment reaction  $\text{CN}^- + \text{H} \rightarrow \text{HCN}(\nu_3) + e^-$ .  $\text{CN}^-$  combining with  $\text{H}$  to form  $(\text{HCN})^-$  follows the solid curve II into the autodetaching region where it is unstable with respect to  $\text{HCN}$  and a free electron.  $\text{CN}^-$  combining with  $\text{H}$  to form  $(\text{CNH})^-$  may follow the dashed curve I.  $(\text{CNH})^-$  is never stable enough to reach the autodetaching region; consequently, it cannot produce  $\text{CNH}$  and a free electron.

region (curve I in Fig. 11). We have no evidence that supports or suggests this mechanism so far.

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## APPENDIX A

### 1. Overtone $A$ factors for $\text{HCN}$

We must have values for the ratios of Einstein  $A$  factors in order to find the relative populations of emitting states.  $A(001-000)$  has been measured<sup>18</sup> to be  $74.1 \text{ sec}^{-1}$  but others,  $A(002-001)$  etc., are not available.

TABLE V. Ratios of  $\text{HCl}$  Einstein coefficients.

Transition	$\mu_{ij}$ (esu cm)	$\nu_{ij}$ ( $\text{cm}^{-1}$ )	$A$ ratio	Estimated ratio
1-0	7.12(-20)	2887.0	...	...
2-1	9.93(-20)	2782.6	1.74	1.79
3-2	11.93(-20)	2679.3	2.24	2.40
4-3	13.40(-20)	2576.8	2.52	2.84

TABLE VI. Estimated  $A$  ratios for  $\text{HCN}$ .

Transition	Observed $\nu_{ij}$ ( $\text{cm}^{-1}$ )	Harmonic transition moments	$A(\nu)$
(001) $\rightarrow$ (000)	3311.4	1	...
(002) $\rightarrow$ (001)	3206.4	2	1.82
(003) $\rightarrow$ (002)	3101.4	3	2.46
(004) $\rightarrow$ (003)	2996.5	4	2.96

This Appendix describes a recipe for estimating the ratios we need

$$A(\nu_3) = A[(\nu_3) - (\nu_3 - 1)] / A[(\nu_3 - 1) - (\nu_3 - 2)]$$

The Einstein  $A$  factor is, essentially, a product of a frequency factor and a dipole matrix element<sup>62</sup>

$$A_{10} = \frac{4}{3h} \left( \frac{2\pi}{c} \right)^3 \nu_{10}^3 |\langle 000 | \mu | 001 \rangle|^2 \quad (\text{A1})$$

In this expression,  $\nu$  is the transition frequency and  $\mu$  is the dipole moment operator. Recall that for the case of an harmonic oscillator, the ratios  $A(\nu_3)$  defined in Eq. (13) become  $A(1)=1$ ,  $A(2)=2$ ,  $A(3)=3$ , and  $A(4)=4$ . This is not a reasonable procedure to follow when treating real, anharmonic molecules. We wish to explore a method that uses the experimental transition frequencies  $\nu$  and approximates the dipole matrix elements  $\mu_{1m}$  with harmonic values. An application of this method to  $\text{HCl}$  is illuminating. Table V lists the observed transition moments<sup>64</sup> and frequencies up to  $\nu=4$ . The ratios of the experimental  $A$  coefficients<sup>64</sup> are listed in the column  $A$  ratio. The last entry has the estimated ratios. As an example, we approximate the  $A_{32}/A_{10}$  ratio as  $(2679.3/2887.0)^3 \times 3$  or about 2.40. This is within 7% of the observed ratio.

Let us employ this procedure to estimate the ratios of Einstein coefficients for the  $\nu_3$  manifold of  $\text{HCN}$ . We use the observed transition frequencies<sup>35</sup> and harmonic matrix elements. These ratios are entered as the last column of Table VI. The final values we will use in Eq. (13) to deconvolute our  $\text{HCN}$  experiments are:  $A(2)=1.82$ ,  $A(3)=2.46$ , and  $A(4)=2.96$ . We estimate that these ratios may be in error by  $\pm 10\%$ .

### 2. The $\text{CNH}$ $A$ factor

We wish to know how bright an infrared emitter  $\text{CNH}$  is. Experimental intensities are not available for this reactive species. We can estimate these in the following manner. Wilson, Decius and Cross<sup>62</sup> write the absorption strength between two states  $|0\rangle$  and  $|1\rangle$  as

$$S = \frac{8\pi^3}{3ch} N_0 \nu_{10} |\mu_{10}|^2 \quad (\text{A2})$$

In this expression,  $N_0$  is the number density of absorbing molecules in state  $|0\rangle$ ,  $\nu_{10}$  is the transition frequency, and  $\mu_{10}$  is the transition moment matrix element.

For a transition involving a nondegenerate normal mode  $Q$ , expression (A2) can be approximated by

$$S \sim \frac{N_0 \pi}{3c} \left( \frac{\partial \mu}{\partial Q} \right)_0^2 \quad (\text{A3})$$

TABLE VII. Interference filter transmission functions  $T(f, \nu_3)$ .<sup>a</sup>

Transition	Filter and (bandwidth $\text{cm}^{-1}$ )			
	WO2644 (4488–3270)	Type 1#4 (3330–3180)	Type 2#15 (3090–2960)	NO3462 (2984–2799)
005 → 004	0.0	0.0	0.01	0.52
004 → 003	0.0	0.0	0.34	0.48
003 → 002	0.01	0.0	0.44	0.05
002 → 001	0.06	0.17	0.04	0.0
001 → 000	0.52	0.52	0.0	0.0

<sup>a</sup>The  $T(f, \nu_3)$  are defined in Eq. (14).

We wish to exploit Eq. (A3) to estimate the absorption strength of  $\text{CNH}(000) \rightarrow (001)$ . Dr. J. J. Wendoloski has evaluated the dipole moment derivatives in Eq. (A3) for both HCN and CNH. This has been carried out with *ab initio* GVB(PP) computer codes. A Gaussian basis set was adopted with sufficient flexibility such that evaluation of the dipole moment derivative for HCN,  $(\partial\mu/\partial Q_3)_{\text{HCN}}$ , leads to a reasonable value of  $S_3$  (see Table III). With this basis set, the dipole moment derivative for CNH was evaluated. It is found that  $(\partial\mu/\partial Q_3)_{\text{CNH}} = 1.8(\partial\mu/\partial Q_3)_{\text{HCN}}$ . From Eqs. (A1 and (A3) together with the frequencies from Table III, we can conjecture a relative value for the Einstein A coefficient for  $\text{CNH}(001) \rightarrow (000)$ ,  $A_{001}(\text{CNH})/A_{001}(\text{HCN}) = 4.0$ .

## APPENDIX B

This appendix collects together several of the properties of our fixed frequency filters. The functions  $T(f, \nu_3)$ , defined in Eq. (14), characterize the filters and are listed in Table VII. Below each filter name is the experimentally determined band pass in  $\text{cm}^{-1}$ . For example, NO3462 transmits light between 2984 and 2799  $\text{cm}^{-1}$ .

Table VIII lists experimentally observed intensities from Reactions (3)–(6). The normalization of emission intensities is arbitrary and varies from reaction to reaction.

TABLE VIII. Observed relative emission intensities.

Reaction	Filter	Relative intensity	Total emission
$\text{CN}^+ + \text{HCl}$	Cold gas ratio	0.19	1.0
$\text{CN}^+ + \text{HBr}$	Cold gas ratio	0.65	2.5
	Type 1#4	1.10	
	Type 2#15	0.25	
$\text{CN}^+ + \text{H}$	Cold gas ratio	0.69	4.2
	Type 1#4	1.08	
	Type 2#15	0.51	
	NO3462	0.24	
$\text{CN}^+ + \text{HI}$	Cold gas ratio	0.90	2.5
	WO2644	2.80	
	Type 1#4	1.00	
	Type 2#15	0.66	
	NO3462	0.13	

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